SONOCHEMISTRY APPROACH FOR A NEW PROCESS BIODIESEL PRODUCTION FROM JATROPHA CURCAS OIL

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ABSTRACT

This thesis presents the sonochemistry approach to reduce required reaction time to convert the Jatropha Curcas oil into biodiesel using an the ultrasound clamp on tubular reactor. The effect of diameter clamp on tubular reactor to remove free fatty acid (FFA) in the esterification process was investigated. The concentrations of methanol and catalyst in the transesterification process were clearly observed in this research. While in the purification process, the water concentration to oil, the output power and reaction time were investigated. The tube of diameter 60 mm removed FFA to below 1 % in 5 minutes. The optimum condition of the transesterification process was a molar ratio of methanol to oil of 7:1, catalyst concentration of 1 %, time of reaction of 5 minutes. Meanwhile the optimum condition of the purification process was at water concentration of 10 % (v/v), power output of 240 W, time of reaction of 5 minutes. The reaction time of esterification by clamp on tubular reactor reduces until 96 %, and transesterification reaction reduces until 83 % compared to conventional stirring method. The small pilot plant has been developed in this research according to the optimum condition. The average energy for one kg of biodiesel needed 0.06 kWh and 11 hour time of production process. In the performance engine and emission, this decreased of the brake specific fuel consumption (BSFC) and brake specific energy consumption (BSEC) could be due to lower heating value and higher density compared to diesel fuel. As an average amount of smoke density, was decreased to 60 % compared to diesel fuel. Average lessening of CO_2 was determined as same as diesel fuel.

ABSTRAK

Tesis ini menggunakan pendekatan *Sonochemistry* dalam mengurangkan masa tindak balas yang diperlukan untuk menukarkan minyak *Jatropha Curcas* kepada biodiesel, dengan menggunakan reaktor tiup yang diapit dengan kaedah ultrasonik. Pengaruh diameter tiup yang diapit dikaji dalam mengasingkan asid lemak bebas (FFA) melalu proses pengesteran. Menerusi penyelidikan ini juga dilakukan kajian nisbah kemolaran metanol kepada minyak *Jatropha Curcas* dan jumlah mankin dalam proses pengtransesteran. Manakala dalam penyelidikan proses pembersihan, kepekatan air kepada minyak, kuasa keluaran dan masa tindak balas telah dikaji. Tiup berdiameter 60 mm telah berjaya mengasingkan FFA kurang dari 1 % dalam masa tindak balas 5 minit. Manakala keadaan optimum untuk proses pengtransesteran adalah didapati pada nisbah kemolaran metanol kepada minyak *Jatropha Curcas* 7:1 dan jumlah mankin sebanyak 1 % dalam masa tindak balas 5 minit. Sementara itu, 10 % kepekatan air kepada minyak (v/v), kuasa keluaran sebanyak 240 W menerusi masa tindak balas selama 5 minit adalah keadaan optimum pada proses pembersihan. Di samping itu, masa tindak balas bagi proses pengesteran menggunakan reaktor tiup yang diapit dengan kaedah ultrasonik berbanding dengan kaedah pengacauan konvensional telah berkurang sehingga 96 % dan bagi proses pengtransesteran telah berkurang sebanyak 83 %. Menerusi penyelidikan ini, satu loji pandu telah dihasilkan berdasarkan keadaan optimum yang tersebut di atas. Hasilnya ialah sebanyak 0.06 kWh purata tenaga diperlukan untuk menghasilkan 1 kg biodiesel dalam tempoh 11 jam. Dalam prestasi enjin dan bahan cemar, pengurangan pengunaan Bahan Api Tentu Brake (BSFC) dan pengunaan Tenaga Tentu Brake (BSEC) mungkin disebabkan oleh nilai pemanasan (LHV) yang rendah dan ketumpatan yang tinggi berbanding bahan api diesel. Bagi purata jumlah ketumpatan asap telah berkurang kepada 60 % berbanding bahan api diesel. Malah purata pengurangan CO_2 juga ditentukan sama seperti bahan api daripada diesel.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	-	Absorbance
a	-	Amplitude
C	-	Carbon
cc	-	Cubic Centimeter
cm	-	Centimeter
g	-	Grams
h	-	Hour
H	-	Hydrogen
hp	-	Horse power
Hz	-	Hertz
kPa	-	KiloPascal
K	-	Kelvin
k	-	Specific Rate of Reaction
kg	-	Kilogram
kHz	-	Kilo Hertz
km	-	Kilometer
kW	-	Kilo watt
lb	-	Pound
m	-	Meter
m^3/s	-	Meter cubic per second
mg	-	Milligrams
MHz	-	Mega Hertz
min	-	Minutes
MJ	-	Mega Joule
ml	-	Milliliters
mm	-	Millimeter
Mol	-	Molar

mol.%	-	Molar Percentage
N	-	Revolution per minutes
Nm	-	Newton meter
^{o}C	-	Degree Celsius
^{o}F	-	Degree Fahrenheit
P_A	-	Pressure Amplitude
pH	-	Potential of Hydrogen
rpm	-	Revolution per minutes
s	-	Second
V	-	Volt
v/v	-	Volume per volume
W	-	Watt
W. cm^{-2}	-	Watt per square centimeter
Wt.%	-	Weight Percentage
µl	-	Micro liter
µm	-	Micrometer
µs	-	Micro second
%	-	Percentage
ABDC	-	After Bottom Dead Center
Approx.	-	Approximately
ATDC	-	After Top Dead Center
atm	-	Atmosphere
ATR	-	Attenuated Total Reflection
BBDC	-	Before Bottom Dead Center
BMEP	-	Brake Mean Effective Pressure
bph	-	Barrel per hour
BSEC	-	Brake Specific Energy Consumption
BSFC	-	Brake Specific Fuel Consumption
BTDC	-	Before Top Dead Center
CI	-	Compression Ignition
CN	-	Cetane number
CH_3OH	-	Methanol
DG's	-	Diglycerides
EN	-	European Norm

FAME	-	Fatty Acid Methyl Ester
FFA	-	Free Fatty Acid
FSWM	-	Frequency Switch Wave Modulation
H_2SO_4	-	Sulfuric Acid
H_3PO_4	-	Phosphoric Acid
KOH	-	Potassium Hydroxide
MG's	-	Monoglycerides
Na_2SO_4	-	Sodium Sulfate
NaOH	-	Sodium Hydroxide
PWM	-	Pulse Width Modulation
SI	-	Spark Ignition
TG's	-	Triglycerides

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CHAPTER I

INTRODUCTION

1.1 Research background

The idea of using vegetable oil as an engine fuel dated back to 1895, when the French-born German engineer Rudolf Christian Karl Diesel (1858-1913), developed the first engine to run on peanut oil, as he demonstrated at the World Exhibition in Paris in 1900. However, using raw vegetable oils for diesel engines during prolonged times could cause numerous engine-related problems. The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking and piston ring sticking (Canakci, 2001).

Walton, in 1938, reported on pioneer work with vegetable oils and suggested an early concept for biodiesel. Soybean oil, palm oil and cottonseed oil were examined in a diesel engine, which utilized 0.416 lb/bph of fuel, similar to a modern engine in efficiency. Steady-state testing showed that soybean oil, palm oil and cottonseed oil all gave fuel economies of 90-91% compared to petroleum diesel at wide open throttle and various speeds. Whole oils were reported to form carbon deposits and exhibited pour point problems; palm oil corroded copper and brass significantly. Because of the difficulties experienced, Walton suggested splitting off the triglycerides and using the resulting fatty acids as fuel (Graboski & McCormick, 1998)

Biodiesel is an alternative fuel for diesel engines that has been receiving great attention worldwide. It is renewable. It can be also used either pure or in blends with diesel fuel in unmodified diesel engines, and it reduces some exhaust pollutants (Jones, 2008). Biodiesel is as well attractive because it can be produced easily from feedstock. In the conventional process, biodiesel is processed by the

transesterfication of oils with methanol in the presence of catalyst, such as alkalis (KOH, NaOH) or their corresponding alkoxides (Freedman *et al*., 1984; Holser & Harry-O'Kuru, 2006; Ma & Hanna, 1999; Jitputti *et al*., 2006).

Biodiesel production in Malaysia depends on the palm oil which is the edible oil. Hence the feedstock alternatives that are non edible oil must be obtained to replace palm oil. Attention turns to Jatropha Curcas which grows in tropical and subtropical climates across the developing world (Openshaw, 2000). Jatropha Curcas oil cannot be used for food purposes (non edible oil) because of its content of a toxalbumine which called curcine and the presence of various toxic phorbol esters, for some of which the structure has recently been elucidated (Haas & Mittelbach, 2000; Hirota *et al*., 1988; Makkar *et al*., 2009; Devappa *et al*., 2010). This plant is adaptable to the large variety of soils, altitude and volume of rain. The plant yields seed oil rich in oleic and linoleic acid (Haas *et al*., 2002). Many scientists are interested in exploring the potential of this plant (Banerji *et al*., 1985; Senthil Kumar *et al*., 2003; Pramanik, 2003; Akintayo, 2004). However, in Jatropha Curcas seed oil extraction, Jatropha Curcas oil is stored at a long time prior to utilization without proper handling and storage. The process causes various chemical reactions such us hydrolysis, polymerizations, and oxidation. Therefore, the physical and chemical properties of the Jatropha Curcas oil change during handling and storage. The presence of free fatty acid (FFA) has been found to increase due to the hydrolysis of triglycerides in the presence of moisture and oxidation (Berchmans & Hirata, 2008). Jatropha Curcas oil with high FFA affects to the final product of alkali base catalyzed transesterification reaction. The high FFA content (>1% w/w) will cause soap formation and the separation of products will be exceedingly difficult, and as a result, it has a low yield of biodiesel product (Goodrum, 2002).

The biodiesel production from Jathropa Curcas consists of three steps namely acid catalyze esterification, followed by base catalyzed transesterification and purification. Berchman and Sahoo reported that the conventional techniques for biodiesel production are based on the use of stirring typically low rates, which are over temperatures of 70–200 ^{o}C, and reaction times of up to one hour for achieving ester content in the range of 90–95 % (Berchmans & Hirata, 2008; Sahoo & Das, 2009). The biodiesel reaction involves two immiscible phases as can be seen by catalyst dissolves in alcohol and oil. Currently, biodiesel was produced by conventional stirring method. However, in the conventional stirring method, the

reaction can occur only interfacial region between the liquids as an alkaline catalyst are essentially insoluble in the oil phase due to of limitation in the mass and heat transfer. This is impacting on the low rates of chemical reactions. Therefore, vigorous mixing and heating using sonochemistry approach are required to increase the area contact between two spaces and causing to increase the rates of reaction.

Since the ultrasound can effectively promote chemical reaction, all experiments were conducted in an ultrasonic reactor (Mason & Lorimer, 2002; Suslick *et al*., 1984; Suslick *et al*., 2003; Colucci *et al*., 2005; Deng *et al*., 2010). Acoustic cavitation is happened due to the ultrasonic reactor. The optimum condition of chemical reaction was affected by acoustic cavitation with the collapse bubble phenomena. Stavarache (2007) reported the transesterification reactions using ultrasonic cleaner bath WS 1200–40, with a total power of 1200 w and working power at 70%. The reaction temperature was 36 ± 2 ^{o}C for all experiments and was maintained constant by circulating water through the bath. The conversion of ester content at the end of 60 minutes of irradiation time was almost the same regardless the type of oil, meaning that the reaction mixture was in a steady state (i.e. equilibrium concentration was reached) (Stavarache *et al*., 2007).

1.2 Problem statement

The conventional techniques for biodiesel production based on use of stirring typically with low rates reaction times of up to 1 h for achieving methyl ester percentage in the range of 90–95 %. The low rates of chemical reaction will influence the cost of biodiesel processing. The ultrasonic process can be one approach for increase the rates of reaction. Recently, many researchers on transesterification of vegetable oils at laboratory scale have reported excellent biodiesel yield by ultrasonic technique (Stavarache *et al*., 2007; Colucci *et al*., 2005; Deng *et al*., 2010). Many types of ultrasonic such as an ultrasonic cleaner and ultrasonic horn, for biodiesel process have been investigated. However, the type of ultrasonic which was used in recently research; it has fixed resonant frequency and output power with the small capacity (below 1 liter). Therefore, the use of an ultrasonic clamp on tubular reactor is one of the alternative tools for increase the

rates of reaction on biodiesel production which have piezoelectric transducers type at a tube with the longitudinal vibration; moreover frequency and output power ultrasonic can be adjustable with capacity of reactor up to 2 liters.

1.3 Research aim

The aim of this research is an increase the rate of reaction on the biodiesel production process from Jatropha Curcas oil using Ultrasonic Clamp on Tubular Reactor.

1.4 Objective

The objectives of this research are:

i. To elucidate the effect of ultrasound by clamp on tubular reactor on the acid catalyzed esterification, alkaline base catalyzed transesterification and purification process.
ii. To identify the optimum conditions on the acid catalyzed esterification, alkaline base catalyzed transesterification and purification process.
iii. To develop a small pilot plant biodiesel production based on sonochemistry approach and to test the biodiesel fuel obtained from Jatropha Curcas oil on diesel engine performance and exhaust gaseous emissions.

1.5 Scope of study

The scopes of this research:

i. Acid catalyzed esterification prosess by using 21 and 60 mm diameter tube of ultrasonic clamp on tubular reactor was used to remove free fatty acid (FFA) and to reduce reaction time.

ii. Alkaline base catalyzed transesterification by using an ultrasonic clamp on tubular reactor was used to reduce reaction time at different operation parameter such as methanol to oil molar ratios, catalyst concentration NaOH.

iii. Comparing on methyl ester content between by using Gas Chromatography according to EN 14130 and by attenuated total reflection (ATR) of methanol to oil molar ratio and catalyst concentration and study phase diagram glycerine-methanol-methyl ester.

iv. Purification process by using an ultrasonic clamp on tubular reactor was used to get pure fatty acid methyl ester at different operation parameter such as output power of water to oil concentration and reaction times.

v. Development small pilot plant based on the optimum process on an alkaline based catalyzed transesterification process using an ultrasonic clamp on tubular reactor and to test the biodiesel from Jatropha Curcas on performance and exhaust emissions.

CHAPTER II

LITERATURE REVIEW

2.1 Jatropha curcas

One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as non edible oils, animal fats, waste food oil and by products of the refining vegetable's oils (Veljkovic *et al*., 2006). Jatropha Curcas oil cannot be used for food purposes since its non edible oil and because of its content of a toxalbumine which called curcine and the presence of various toxic phorbol esters, for some of which the structure has recently been elucidated (Haas & Mittelbach, 2000; Hirota *et al*., 1988; Makkar *et al*., 2009; Devappa *et al.*, 2010), which grows in tropical and subtropical climates across the developing world (Openshaw, 2000). The Jatropha Curcas seed is shown in Figure 2.1.

Figure 2.1: Jatropha curcas seed (New Energy and Fuel, 2008)

Jatropha Curcas plant originated from Mexico and has been spread to the tropical and subtropical countries with mainly grown in Asia and Africa. It grows extremely fast and during a span of 4-5 years which it attains a height of around 4 meters. Jatropha Curcas plant starts to produce seeds within one years of cultivation and keeps on producing until the age of 50 years. Jatropha Curcas grows best on well drained soils with good aeration but also well adapted to marginal soils with low nutrient content as well as shallow fields and rocky terrains (Gubitz *et al*, 1997). Comparison the belt area of cultivation between Jatropha Curcas and oil palm is shown in Figure 2.2. The belt area of cultivation Jatropha Curcas is larger than the oil palm.

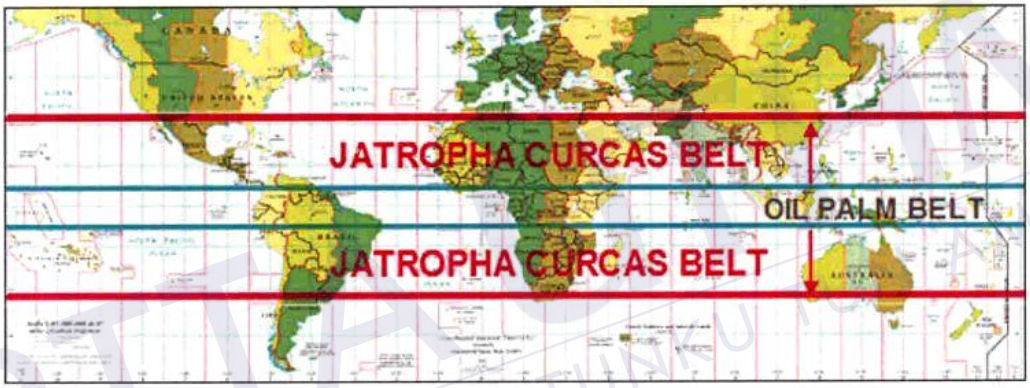

Figure 2.2: The belt area for cultivation of Jatropha Curcas and oil palm (*Jongschaap et.al., 2007)*

The wood and fruit of Jatropha Curcas can be used for numerous purposes, including fuel. The seeds of Jatropha Curcas contain viscous oil, which can be used for manufacture of candles and soap, in cosmetics industry, as a diesel/paraffin substitute or extender. This latter use has important implications for meeting the demand for rural energy services and also exploring practical substitutes for fossil fuels to counter greenhouse gas accumulation in the atmosphere. These characteristics along with its versatility make it of vital importance to developing countries (Kumar & Sharma, 2008). The detailed of benefits obtained from Jatropha Curcas is shown in Figure 2.3.

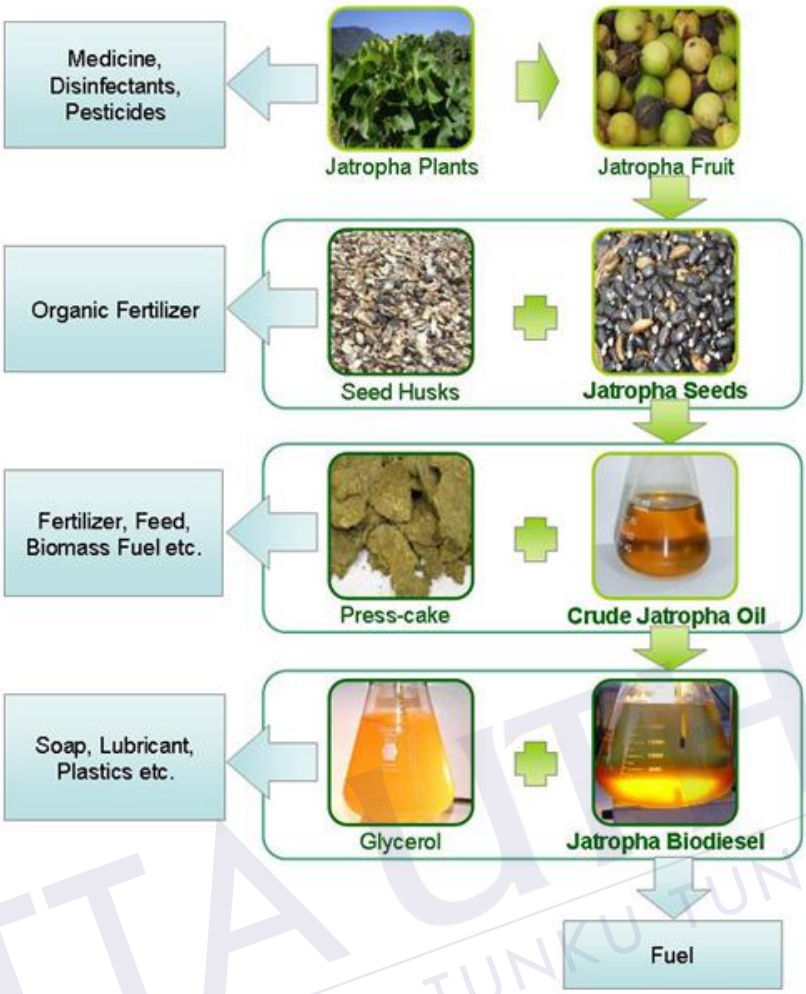

Figure 2.3: The benefits of Jatropha Curcas (Gubitz *et al*, 1997)

Jatropha Curcas prefers temperatures averaging 68-85 ^{o} F (20-28 ^{o} C). The plant flowers between September and November and the fruits come from October to December. Recommended planting rates of Jatropha Curcas are 2,000 / 2,500 plants per hectare (2.5 acres), this will produce, depending on density and quantity, 3-10 tones of Jatropha seed. Fruit of Jatropha is green capsule shaped, and contains 3 to 4 seeds. One tonne of Jatropha Curcas seeds will produce approximately 350-550 liters of biodiesel, while the residue can also be processed into biomass to power electricity plants. The plant can be used to prevent and/or control erosion, to reclaim land, grown as a live fence, especially to contain or exclude farm animals and be planted as a commercial crop. It is a native of tropical America, but now thrives in many parts of the tropics and sub-tropics in Africa/Asia (Gübitz *et al*., 1999; Kumar

& Sharma, 2008; Openshaw, 2000 ; Herrera *et al*., 2006). Plant of Jatropha Curcas cultivation in Sabah Malaysia is shown in Figure 2.4.

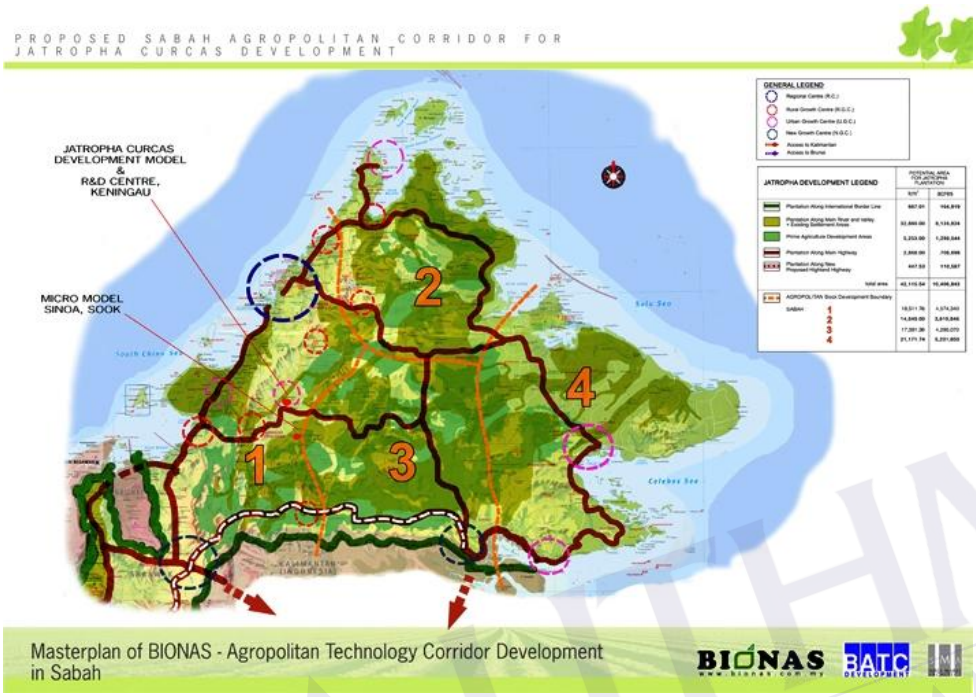

Figure 2.4: The plant of Jatropha Curcas cultivation in Sabah Malaysia (Bionas, 2007)

2.2 Biodiesel

Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide. Although it attracts the most attention because it is renewable, it can be used either pure or in blends with diesel fuel in unmodified diesel engines, and it reduces some exhaust pollutants. It is also attractive because it can be produced easily from common feedstock's. However, the relative simplicity of biodiesel production can disguise the importance of maintaining high quality standards for any fuel supplied to a modern diesel engine. It is essential to the growth of the biodiesel industry that all fuel produced and sold meet these quality standards. Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, designated B100 (Van Gerpen *et al*., 2004).

All natural fats and oils are esters of fatty acids and glycerol. These are known as glycerides or triglycerides (TG's). With few exceptions, the carboxylic acids (fatty acids) from which the fats and oils are derived are all straight-chain compounds ranging in size from 3 to 18 carbons (Van Gerpen *et al*., 2004). Figure 2.5 shows the molecular structure of oleic acid (C18:0). This TG's has a molecular weight of 282 g/g-mol and it is found in Jatropha Curcas oils.

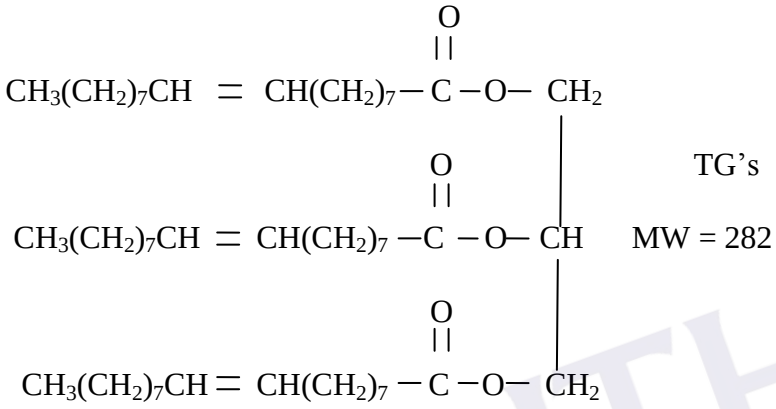

Figure 2.5: Molecular structure of triolein, a triglyceride of the oleic acid (C18:1)

The chemical composition of fat and oil esters is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. Table 2.1 shows the chemical structure of the fatty acid chains found in the most common biodiesel source materials Graboski & McCormick, 1998).

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Table 2.1: Chemical structure of common fatty acid and their methyl ester (Graboski & McCormick, 1998)

Fatty acid	Structure	Common acronym	Methyl ester
Palmitic acid	$R\text{-}(CH_2)_{14}\text{-}CH_3$	C16:0	Methyl palmitate
Stearic acid	$R\text{--}(CH_2)_{16}\text{-}CH_3$	C18:0	Mehyl stearate
Oleic acid	$R\text{-}(CH_2)_7\text{-}CH{=}CH\text{--}(CH_2)_7\text{-}CH_3$	C18:1	Methyl oleate
Linoleic Acid	$R\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$	C18:2	Methyl linoleate
Linolenic Acid	$R\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2)_3\text{-}CH_3$	C18:3	Methyl linolenate

The list of characteristic the most common fatty acids and their corresponding methyl as shown in Table 2.2 (Graboski & McCormick, 1998).

Table 2.2: The characteristics of common fatty acids and their methyl esters (Graboski & McCormick, 1998)

Fatty acid *Methyl ester*	Formula	Molecular weight	Melting Point (^{o} C)
Palmitic acid	$C_{16}H_{32}O_2$	256.428	63-64
Methyl palmitate	*$C_{17}H_{34}O_2$*	*270.457*	*30.5*
Stearic acid	$C_{18}H_{36}O_2$	284.481	70
Methyl stearate	*$C_{19}H_{38}O_2$*	*298.511*	*39*
Oleic acid	$C_{18}H_{34}O_2$	282.465	16
Methyl oleate	*$C_{19}H_{36}O_2$*	*296.495*	*-20*
Linoleic acid	$C_{18}H_{32}O_2$	280.450	-5
Methyl linoleate	*$C_{19}H_{34}O_2$*	*294.479*	*-35*
Linolenic acid	$C_{18}H_{30}O_2$	278.434	-11
Methyl linoleate	*$C_{19}H_{32}O_2$*	*292.463*	*-52/-57*

The major fatty acids in Jatropha Curcas oil were the oleic, linoleic, palmitic and the stearic fatty acid. Oleic acid showed the highest percentage of composition of 42.8 % followed by linoleic acid with 32.8 %. Thus, Jatropha Curcas oil can be classified as oleic–linoleic oil. Jatropha Curcas oil has the highest oleic contain than palm oil, palm kernel, sunflower, coconut and soybean oil as shown in Table 2.3. Jatropha oil seed only consists of 0.2 % linolenic acid, which is lower compared to the sunflower oil and palm oil is shown in Table 2.3 (Edem, 2002).

Tabel 2.3: Fatty acid composition in different feedstock (wt.%) (Edem, 2002)

Fatty Acid	Jatropha curcas oil	Palm kernel oil	Sunflower oil	Soybean oil	Palm oil
Oleic 18:1	44.7	15.4	21.1	23.4	39.2
Linoleic 18:2	32.8	2.4	66.2	53.2	10.1
Palmitic 16:0	14.2	8.4	-	11.0	44.0
Stearic 18: 0	7.0	2.4	4.5	4.0	4.5
Palmitoliec 16 :1	0.7	-	-	-	-
Linolenic 18:3	0.2	-	-	7.8	0.4
Arachidic 20:0	0.2	0.1	0.3	-	-
Myristic 14:0	0.1	16.3	-	0.1	1.1

There are two major biodiesel standards that are most referred to, namely, the European Standard for Biodiesel (EN 14214) and the American Standard

Specifications for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels (ASTM 6751). The biodiesel fuel standard EN14214 was given in Table 2.4. According to the European standard, the concentration of linolenic acid and acid value, biodiesel should not exceed the limit of 12% and 1%, respectively.

Table 2.4: Detailed requirement of biodiesel according to European Standard EN14214 (European Committee for Standard, 2003)

Property	Unit	Limits		Test methods
		Minimum	Maximum	
Ester Content	% (mm^{-1})	96.5		EN 14103
Density at 15^{o}C	kg m^{-1}	860	900	EN ISO 3675
Viscosity at 40^{o}C	mm^2s^{-1}	3.5	5	EN ISO 3104
Flash point	^{o}C	120	-	ISO 3679
Acid value	mg KOH g^{-1}		0.5	EN 14104
Cetane index		510	-	EN ISO 5165
Sulphur content	mg kg^{-1}	-	10	-
Sulphated ash content	%(mm^{-1})	-	0.02	ISO 3987
Water content	mg kg^{-1}	-	500	EN ISO 12937
Total contamination	mg kg^{-1}	-	24	EN 12662
Copper strip corrosion (3 hr at 50^{o}C)	rating	1	-	EN ISO 2160
Oxidation stability 110^{o}C	hr	6.0	-	EN 14112
Iodine value	-	-	120	EN 14111
Linolenic acid methyl ester	% (mm^{-1})	-	12	EN 14103
Methanol content	% (mm^{-1})	-	0.2	EN 14110
Monoglyceride content	% (mm^{-1})	-	0.8	EN 14105
Diglyceride content	% (mm^{-1})	-	0.2	EN 14105
Triglyceride content	% (mm^{-1})	-	0.2	EN 14105
Free glycerol	% (mm^{-1})	-	0.02	EN 14105
Total glycerol	% (mm^{-1})	-	0.025	EN 14105
Alkaline content (Na+K)	mg kg^{-1}	-	5	EN 14108
Phosporous content	mg kg-1	-	10	EN 14107

Meanwhile the biodiesel fuel standard ASTM D 6751 was given in Table 2.5.

Table 2.5: Detailed requirement of biodiesel according to ASTM D6751 (ASTM, 2003)

Property	Unit	Grade S15	Grade S500	Test method
		Limits	Limits	
Kinematic viscocity at 40°C	mm^2s^{-1}	1.9-6.0	1.9-6.0	ASTM D445
Flash point(closed up)	°C	130.0 min	130.0 min	ASTM D93
Sulphur content	% mass	0.0015 max	0.05 max	ASTM D5453
Carbon residu	% mass	0.050 max	0.050 max	ASTM D4530
Acid number	mg KOH g^{-1}	0.8 max	0.8 max	ASTM D664
Cloud point	°C	Report*	Report*	ASTM D2500
Cetane number	-	47 min	47 min	ASTM D613
Sulphated ash content	% mass	0.020 max	0.020 max	ASTM D874
Water and sediment	% volume	0.050 max	0.050 max	ASTM D1796
Copper strip corrosion	rating	No. 3 max	No.3 max	ASTM D130
Free glycerol	% mass	0.020	0.020	ASTM D6584
Total glycerol	% mass	0.240	0.240	ASTM D6584
Phosphorus	% mass	0.001 max	0.001 max	ASTM D4951
Distillation temperature	°C	360 max	360 max	ASTM D1160

Note * : The cloud point of biodiesel is generally higher than that of petroleum-based diesel fuel and should be taken into consideration when blending

Biodiesel production with high free fatty acid feedstock consists of acid catalyzed esterification followed by alkaline base catalyzed and purification process.

2.3.1 Acid catalyzed esterification

Acid catalysis offers the advantage of esterification free fatty acids contained in the fats and oils and therefore, is especially suited for the transesterification of highly acidic fatty materials. However, acid-catalyzed transesterifications are usually far slower than alkali catalyzed reactions and require higher temperatures and pressures

as well as higher amounts of alcohol. The typical reaction conditions for homogeneous acid-catalyzed methanolysis are temperatures of up to 100°C and pressures of up to 5 bars in order to keep the alcohol in a liquid form (Lepper & Friesenhagen, 1984). A further disadvantage of acid catalysis probably prompted by the higher reaction temperatures and increased the formation of unwanted secondary products, such as dialkylethers or glycerol ethers (Mittelbach *et al*., 1996). Because of the slow reaction rates and high temperatures needed for transesterification, acid catalysts are only used for esterification reactions. Thus for vegetable oils or animal fats with an amount of free fatty acids larger than approximately 1 % two strategies are possible. The free fatty acids (FFA) can be esterified under acid catalyzed conditions followed by alkaline catalyzed transesterification reaction. This so called esterification has the advantage that prior to the transesterification most of the free fatty acids is already converted into methyl ester, accordingly the overall yield is very high.

Figure 2.6 shows the oils with high contents of FFA, converted into biodiesel via acid esterification using sulfuric acid as a catalyst.

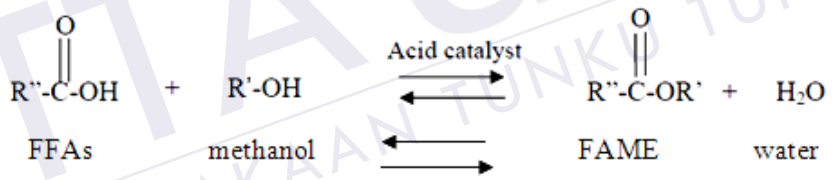

Figure 2.6: Acid esterification of FFA with methanol to produce methyl esters and water (Lepper & Friesenhagen, 1984)

A new technique has been developed to produce biodiesel from Jatropha Curcas seed oil having high free fatty acids (15 % FFA). The high FFA level of Jatropha Curcas oil was reduced to less than one % by a two-step pretreatment process. The first step was carried out with 0.60 wt.% methanol-to-oil ratio in the presence of 1 wt.% H_2SO_4 as an acid catalyst in 1 h reaction at 50 ^oC. After the reaction, the mixture was allowed to settle for 2 h and the separated methanol–water mixture at the top layer was removed (Berchmans & Hirata, 2008). Esterification of free fatty acids occurs simultaneously with the transesterification reaction of triglycerides.

2.3.2 Alkaline base catalyzed transesterification

Biodiesel manufactured in batch or continuous systems by transesterification, also called alcoholysis or interesterification as shown in Figure 2.7. In transesterification, one ester is converted to another. The reaction is catalyzed by either acid or base and involves a reaction with an alcohol.

Alkaline or basic catalysis is by far the most commonly used reaction type for biodiesel production. The main advantage of this form of catalysis over acid catalyzed transesterifications is a high conversion under mild conditions in comparatively short reaction times (Freedman *et al.*, 1986). It was estimated that under the same temperature conditions and catalyst concentrations methanolysis might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent (Formo, 1954). Moreover, alkaline catalysts are less corrosive to industrial equipment, and thus enable the use of less expensive carbon-steel reactor material.

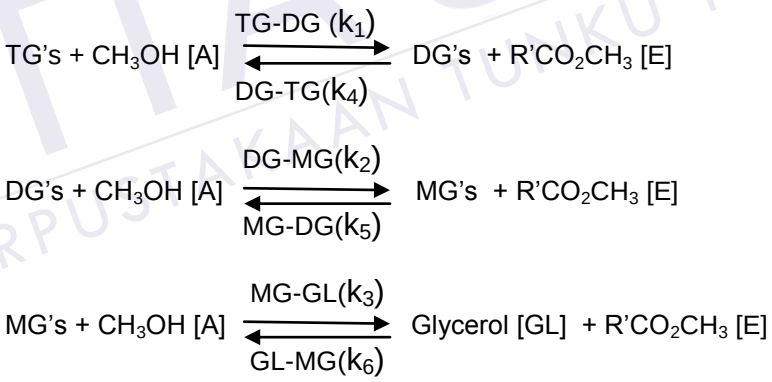

Figure 2.7: Transesterification of tryglycerides with alcohol to produce glycerol and alkyl esters (Darnoko & Cheryan, 2000)

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, and butanol. Methanol and ethanol are used most frequently, especially for methanol due to its low price and its physical and chemical advantages – polar and shortest chain alcohol (Ma & Hanna, 1999). Branched-chain alcohols, such as isopropyl and 2-butyl have been used in

transesterifications of oils and fats in order to reduce the crystallization temperature of biodiesel (Lee *et al*., 1995).

Alkaline transesterification is strongly influenced by free fatty acids (FFA), and water content in the raw material. FFA and water content should be kept below 0.5 % and 0.06 %, respectively to minimize side reactions. At slightly above room temperature this reaction proceeds to conversion of 90-97%, in an excess of methanol, within approximately one hour. The remaining 3-10 % is glycerol, mono/di/triglycerides, and free fatty acids. Much of the free fatty acid is converted to soap (sodium or potassium salt of the fatty acid) and water.

The alkali-catalyzed reaction mechanism consists of three steps. The first step is an attack on the carbonyl carbon atom of the triglycerides (TG's) molecule by the anion (the methoxide ion) to form a tetrahedral intermediate. In the second step, this intermediate reacts with the methanol to regenerate the anion. In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglycerides (DG's). When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalyst alkoxide group is formed. A small amount of water generated in the reaction may cause soap formation during transesterification (Ma & Hanna, 1999).

Berchman H.J and Hirata S, 2008 reported a technique to produce biodiesel from Jatropha Curcas seed oil having high free fatty acids (15% FFA) has been developed. The high FFA level of Jatropha Curcas oil was reduced to less than 1% by a two-step pretreatment process. The second step was transesterified using 32.56 wt.% methanol to oil or same with methanol to oil molar ratio 9:1 and 1.4 wt.% NaOH to oil as an alkaline catalyst to produce biodiesel at 65 ^{o}C. The final yield for methyl esters of fatty acids was achieved at 90% in two hours (Berchmans & Hirata, 2008).

The batch transesterification of vegetable oil with methanol, in the presence of potassium hydroxide as a catalyst, by using low frequency ultrasound cleaner batch (40 kHz) was studied with the aim of gaining more knowledge on the intimate reaction mechanism. The conversion of methyl ester content at the end of between 30- 60 minutes of sonification were almost same regardless the type of oil, meaning that the reaction mixture was in the steady state (i.e. equilibrium concentration was reached) (Stavarache *et al*., 2005; Stavarache *et al*., 2007; Stavarache *et al*., 2007; Singh *et al*., 2007; Colucci *et al*., 2005; Deng *et al*., 2010).

2.3.3 Purification

Purification or washing is an important process to get pure methyl ester. Unreacted methanol from the transesterification process in the biodiesel fuel can result in fire or explosion and can corrode engine components. The catalyst, sodium hydroxide, can also attack other engine components. Since the methanol and sodium hydroxide are chemical bases, unwashed biodiesel is caustic and may damage diesel engine components. Purification consists of conventional techniques and new purification techniques. Water washing is generally accomplished to remove soap, catalyst, methanol and other contaminants from biodiesel, using deionized water. Chongkhong *et al* (2009) investigated a neutralization technique instead of distillation to purify the oil transesterification. The process was carried out using three molars of sodium hydroxide in water. Then 2 wt.% of sodium chloride was dissolved in the solution to remove the soap formation. Water at 60-80 ^{o}C was used to wash the ester phase which was allowed to settle and then heated to evaporate from residual water (Chongkhong *et al*., 2009). Jaya et al.(2009) indicated a simple filtration of cation-exchange resins catalyst in the production of biodiesel. The ester layer separated was washed with hot deionized water and dried over anhydrous sodium sulfate (Na_2 SO_4) (Jaya *et al*., 2009). Ferella et al (2010) reported that the formation of soap due to neutralization of FFA in the vegetable oil or triglyceride by potassium hydroxide decreases biodiesel yield and quality. In addition separation of biodiesel and glycerol underwent simple centrifugation and washing product leads to be high utilization of time and water (Ferella *et al*., 2010).

Suprihastuti & Aswati (2007) conducted an experimental biodiesel washing with water extraction. The process showed that washing biodiesel by water extraction in a single stage stirred tank reduced the glycerol content from 0.9331% to at least 0.09% for 20 minutes washing time by adding 50 % water of biodiesel volume. When the water was 300 % of biodiesel volume the glycerol content was less than 0.05 % and the pH was 7.3. To achieve the standard requirement of glycerol content in biodiesel to be less than 0.02 %, the washing was carried out in the multistage process. It was also noted that the rate of mass transfer of glycerol from the biodiesel into water was affected by the temperature of extraction and the volume ratio of solvent to biodiesel. Higher mass transfer rate was achieved on higher bio-diesel to water volume ratio as well as higher temperature. The more water added

the larger the mass transfer area, so the higher volumetric mass transfer coefficient. The higher washing temperature gave higher diffusively of glycerol from biodiesel to water phase, then the mass transfer coefficient was higher (Suprihastuti & Aswati, 2007).

The membrane equipments and ultrasound mostly produced for the purification of crude biodiesel seem to exhibit several advantages over the conventional ones such as eradication/minimization of higher capital cost and other related costs of production, and provide high specific area of mass transfer.

Operations involving membrane technologies in the last years have shown their potentialities in the rationalization of production systems (Drioli & Giorno, 2009). Membrane performance is usually governed by: selectivity or separation factor and permeability. In the absence of defects, the selectivity is a function of the material properties at given operating conditions. The productivity is a function of the material properties as well as the thickness of the membrane film, and the lower the thickness, the higher the productivity (Lu *et al*., 2007 ; Dube *et al* (2007) developed a membrane reactor that removed unreacted vegetable oil from the fatty acid methyl ester (FAME) product after transesterification, yielding high-purity biodiesel and shifting the reaction equilibrium to the product side. The authors stated that the novel membrane process was particularly useful in removing unreacted canola oil from the FAME product yielding a high-purity biodiesel (Dubé *et al*., 2007). Additionally, a novel refining method using membrane extraction was developed by (He *et al*., 2006).

The limited of literature and research to investigate ultrasound purification provides an opportunity to researchers to conduct further investigations on this subject.

2.4 Basic plant equipment in biodiesel production

The basic plant's equipments are used in biodiesel production are reactors, pumps, settling tanks, centrifuges, distillation columns, and storage tanks.

The reactor is the only place in the process where chemical conversion occurs. Reactors can be grouped into two broad categories, batch reactors and

continuous reactors. In the batch reactor, the reactants are fed into the reactor at the determined amount. The reactor is then closed, and the desired reaction conditions are set. The chemical composition within the reactor changes with time. The construction materials are an important consideration for the reactor and storage tanks. For the alkaline base-catalyzed transesterification reaction, stainless steel is the preferred material for the reactor (Van Gerpen *et al*., 2004).

Key reactor variables that dictate conversion and selectivity are temperature, pressure, reaction time (residence time), and degree of mixing. In general, increasing the reaction temperature increases the reaction rate and, hence, the conversion for a given reaction time. Increasing the temperature in the transesterification reaction does impact the operating pressure.

Two reactors within the continuous reactor category are continuous stirred tank reactors (CSTRs) and plug flow reactors (PFRs). CSTR also known as a backmix reactor is shown in Figure 2.8. CSTRs are a common ideal reactor type in chemical engineering. For CSTRs, the reactants are fed into a well-mixed reactor. The composition of the product stream is identical to the composition within the reactor. Hold-up time in a CSTR is given by a residence time distribution.

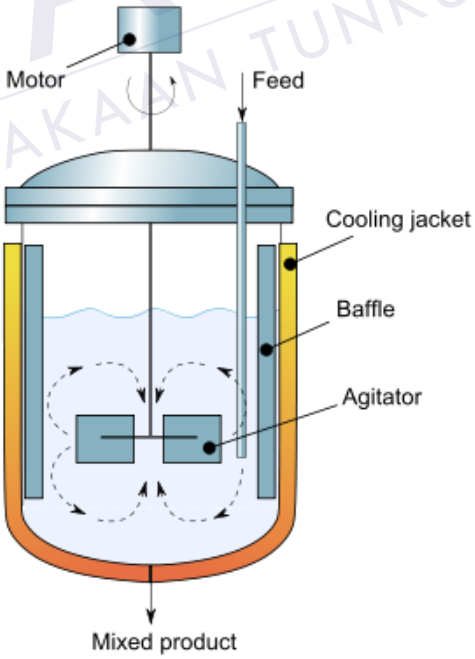

Figure 2.8: Continuous stirred tank reactor (Van Gerpen *et al*., 2004)

The plug flow reactors (PFRs) model is used to describe chemical reactions in continuous, flowing systems. A PFR is a vessel through which flow is continuous,

usually at a steady state, and configured so that conversion of the chemicals and other dependent variables are functions of position within the reactor rather than of time. In the ideal tubular reactor, the fluids flow as if they were solid plugs or pistons, and reaction time is the same for all flowing material at any given tube cross section. PFRs resemble batch reactors in providing initially high driving forces, which diminish as the reactions progress down the tubes. PFR also sometimes called Continuous Tubular Reactors (CTR) is shown in Figure 2.9. For PFRs, the reactants are fed into one side of the reactor. The chemical composition changes as the material moves in plug flow through the reactor (Van Gerpen *et al*., 2004).

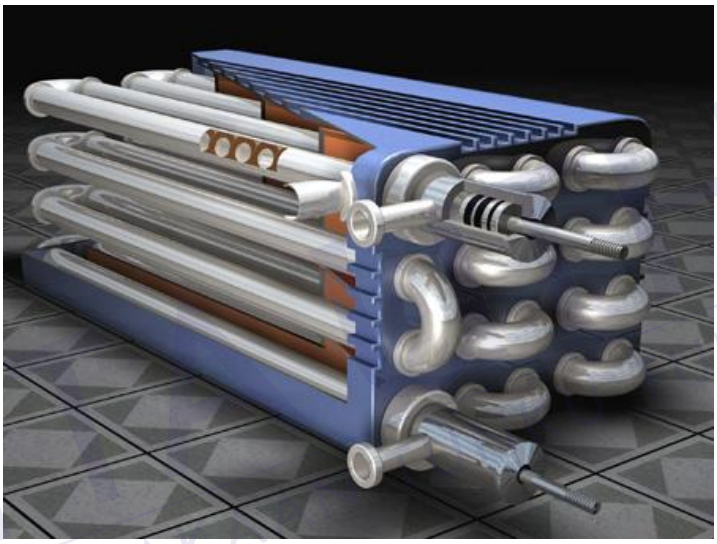

Figure 2.9: Plug flow reactor (Van Gerpen *et al*., 2004)

The pumps play the key role in moving chemicals through the manufacturing plant. The most common type of pump in the chemical industry is a centrifugal pump. The primary components of a centrifugal pump are a shaft, a coupling attaching the shaft to a motor, bearings to support the shaft, a seal around the shaft to prevent leakage, an impeller, and a volute, which converts the kinetic energy imparted by the impeller into the feet or head. The gear pumps are generally used in biodiesel plants. There are a number of different types of positive displacement pumps, including gear pumps (external and internal) and lobe pumps. External gear pumps generally have two gears with an equal number of teeth located on the outside of the gears, whereas internal gear pumps have one larger gear with internal teeth and a smaller gear with external teeth (Van Gerpen *et al*., 2004).

The separation of biodiesel and glycerin can be achieved using a settling tank. While a settling tank may be cheaper, a centrifuge can be used to increase the rate of separation relative to a settling tank. Centrifuges are most typically used to separate solids and liquids, but they can also be used to separate immiscible liquids of different densities. In a centrifuge separation is accomplished by exposing the mixture to a centrifugal force. The denser phase will be preferentially separated to the outer surface of the centrifuge. The choice of appropriate centrifuge type and size are predicated on the degree of separation needed in a specific system.

An important separation device for miscible fluids with similar boiling points (*e.g.*, methanol and water) is the distillation column. Separation in a distillation column is predicated on the difference in volatilities (boiling points) between chemicals in a liquid mixture. In a distillation column, the concentrations of the more volatile species are enriched above the feed point and the less volatile species are enriched below the feed point.

2.5 The new potential technology processing using ultrasound

The earliest form of an ultrasonic transducer was a whistle developed by Francis Galton (1822 ± 1911) in 1883. Galton investigated the threshold frequency of human hearing (Galton, 1883). As well as inventing the whistle that carries his name, Galton explored and helped map a portion of the African interior, invented the weather map and developed the first workable system for classifying and identifying fingerprints. The whistle was part of his study of sensory perception, in this case to determine the limits of hearing in terms of sound frequencies in both humans and animals.

The first commercial application of ultrasonic appeared around 1917 and was the first echo-sounder invented and developed by Paul Langevin. Langevin was noted for on the molecular structure of gases, analysis of secondary emission of X-rays from metals exposed to radiation and for his theory of magnetism (Langevin, 1905). However, Langevin is more generally remembered for important work on piezoelectricity and on piezoceramics (Langevin & Abraham, 1905).

In the present day industrial enterprises continuously increase a tempo of industrial production. Usually, for this purpose it is necessary to modernize or

completely to change the process flow sheet. It is widely known, that using of high intensity ultrasonic oscillations allows intensifying many technological processes, such us extraction, transesterification, emulsification, washing and clearing. The majority of chemical reaction increases under action of an acoustic field and that some reaction do not pass without action of ultrasonic oscillations (Leonov *et al*., 1998).

2.5.1 Sound frequency ranges

The sound of frequencies is recorded in units of Hertz (1 Hertz 1 cycle per second) and the frequency range is shown in Figure 2.10 (Mason & Lorimer, 2002). The range of human hearing is from about 20 Hz to 20 kHz (the upper limit reduces with age). The hearing threshold is not the same for other animal species thus dogs respond to ultrasonic whistles, and bats use frequencies well above 50 kHz for navigation. Ultrasound itself is defined in terms of human hearing and is sound having a frequency higher than that to which the human ear can respond above 18 kHz. The upper limit of ultrasonic frequency is one that is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids. The uses of ultrasound within this large frequency range may be divided broadly into two areas.

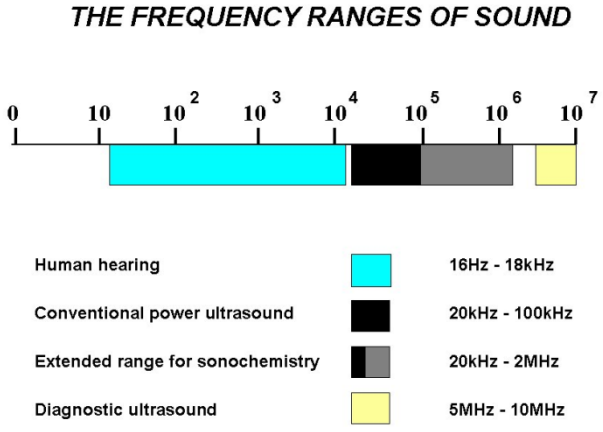

Figure 2.10: Sound frequency range (Mason *et al*, 2002)

The first area involves low amplitude (higher frequency) sound and is concerned with the physical effect of the medium on the wave and is commonly referred to as low power or high frequency ultrasound. Typically, low amplitude waves are used for analytical purposes to measure the velocity and absorption coefficient of the wave in a medium in the range of 2 to 10 MHz range. Information from such measurements can be used in medical imaging, chemical analysis and the study of relaxation phenomena.

Sonochemistry normally uses frequencies between 20 and 40 kHz simply because this is the range employed in common laboratory equipment. However, since acoustic cavitation in liquids can be generated well above these frequencies, recent researches into sonochemistry use a much broader range. High frequency ultrasound from around 5MHz and above does not produce cavitation and this is the range used in medical imaging.

2.5.2 Sound and its influence in sonochemistry

Sound can be explained as a wave of energy transmitted through a medium by vibrating molecules. The vibrating molecules at one end of the medium propagate their vibrational motion to the other end of the medium through pressure differences. Pressure differences occur in cycles, forming pressure waves that can be viewed in two distinct portions: compression and stretching (rarefaction). The rarefaction in a liquid affects to the adhesive capabilities of the liquid. Beside that the rarefaction causes the mean molecular distance of the liquid to increase from the localized decrease in pressure. Because that the decrease in pressure is much less than the static pressure of the liquid and the liquid is not being subjected to a vacuum, rarefaction is referred to as the negative pressure portion of the pressure wave (Sweet, 1998). Figure 2.11 explained that sinusoidal wave illustrating the pressure effects of sound in a given direction.

The x axis is the time a specific region in a solution is under acoustic stress, and the y axis is the pressure change relative to the static (atmospheric) pressure of the solution. The ordinate show that the solution under atmospheric pressure. The bottom portion of the wave explains a rarefaction or negative pressure in the medium

(the pressure of the solution in this region is much less than the static pressure of the solution). While the top of the wave indicate a compression or positive pressure occurring at a given point in the medium (pressure in much greater than the static pressure of the existing atmosphere). As the wave crosses the axis, the system is in equilibrium with the surroundings (the system is under the static pressure of the existing atmosphere) (Sweet, 1998).

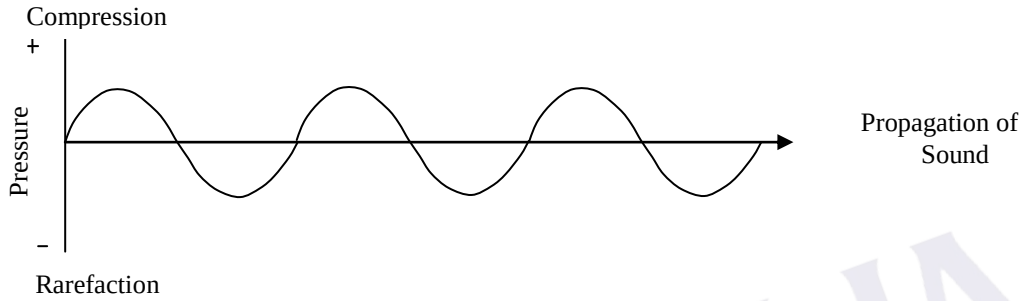

Figure 2.11: Sinusoidal wave illustrating the pressure effects of sound in a given direction (Sweet, 1998)

Ultrasonically-induced cavitation is the formation, growth and violent collapse of bubbles formed by coupling the pressure waves of ultrasound with a liquid (Flynn, 1964). The acoustic stress applied must be greater than the tensile strength of the liquid in order to form the bubble. The water a negative pressure of 10000 atmospheres (atm) is required to shear two layers of water to produce a cavity or bubble (assuming a 10^{-5} cm critical distances among water molecules) in order to induce cavitation. Acoustic stress does not produce a large enough pressure difference to exceed 10000 atmospheres. Evaporation of water lowers the amount of energy necessary to shear two layers of water. This reduction in energy is enough to cause an order of magnitude reduction in the amount of negative pressure required for shearing. Even at 1000 atmospheres a negative pressure, acoustic stress is still insufficient to produce cavitations.

The disruptions in the liquid layer must be present for cavitations to occur through acoustic stress. Influences such as undissolved gases, suspended gas bubbles, organic double layers and particulate matter substantially reduce the tensile strength of the liquid to a point where acoustic stress can cause bubble formation (Yount, 1982 ; Crum, 1979).

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